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(54) Biodegradable foil

(57) The invention relates to a foil comprising a biodegradable polymer base foil to which a coating layer of natural material is applied, which coating layer lowers the permeability of the base foil to oxygen and water vapor. The invention additionally relates to a process for the production of the said foil, as well as to the application of the same to the production of a packaging material.

NL C 1006548

The contents of this patent are in agreement with the description, the claim(s), and any possible diagrams that were originally submitted.

Title: **Biodegradable foil**

The invention relates to a foil comprising a base foil to which a coating layer is applied.

The problems of streams of refuse, both from industry as well as from private households, have become a major concern during the past few decades. The garbage that is produced largely consists, particularly in the last group, of packaging materials that have fulfilled their purpose and have accordingly been discarded. These materials cause considerable stress on the environment.

Different solutions have already been proposed in order to limit this stream of refuse. Examples of this appear in the area of waste prevention and recycling, among others. In addition to these two areas, the search for alternative materials has also received a great deal of attention as a possible solution for the problems of garbage. There has been considerable investment in research in this area, both inside research institutes and universities as well as within corporate life.

Various new materials, which entail less stress for the environment when they later return there, have originated from such investigations. These materials have the characteristic that they are broken down into substances which are preferably soluble in water and are not toxic within a relative short time. The decomposition can take place through hydrolytic splitting, or through the influence of light, air, water, and/or microorganisms which occur in nature, among others. Because of this characteristic, such materials are termed "biodegradable materials".

Polymer materials that are based upon starch or lactic acid, for example, are examples of biodegradable materials that have sufficiently favorable characteristics to be able to be used as packaging materials. A number of the materials based upon one of these two substances are even edible for humans. One example is provided by trays made from a plastic on the basis of starch which are used for snacks, and which can be eaten after the consumption of the enclosed snack. Garbage disposal bags made of biodegradable material have likewise been brought into commercial trade.

In regard to the biodegradability, the most important characteristic of these materials for the stated applications is tightness against fluids. Both for garbage disposal bags as well as for trays for snacks, it is most important for the consumer that the fluids inside the package continue to remain there. Other characteristics can play an important role in the packaging of other materials. During the packaging of various goods, oxygen and water vapor (liquid) must be excluded because of the sensitivity of the goods. In this connection, one should think of coffee, walnuts, tobacco, and the like.

At the same time, a product such as coffee vacuum-packed in a foil of metallized PET, for example, has been brought into commercial trade. This foil is extraordinarily tight against oxygen and water vapor, so that the coffee packaged is

usable for months. The current biodegradable materials, however outstandingly impermeable to water and fluid, can not effectively withstand the gases, such as oxygen and water vapor, in order to keep such a product usable long enough when it is packaged in the same.

The invention is intended to create a foil which can be applied to the production of packaging materials for goods that are sensitive to oxygen and/or water vapor, which foil does not cause any unacceptable stress to the environment when it disappears into nature by way of waste recycling after use.

The invention thus relates to a foil comprising a polymer, biodegradable base foil to which a coating layer of natural material is applied, which coating layer lowers the permeability of the base foil to oxygen and water vapor.

It has been found, surprisingly enough, that a foil in accordance with the invention fulfills the objectives formulated hereinabove. A foil in accordance with the invention can be degraded sufficiently easily by the microorganisms that are normally present in nature in order to be able to return to the environment without unacceptable consequences. In addition, a foil in accordance with the invention has a sufficiently low permeability to oxygen and water vapor in order to be able to serve as a base material for the production of packaging materials for goods which are sensitive to oxygen and/or water vapor. It has been shown that such types of goods can be preserved sufficiently long in a package produced from a foil in accordance with the invention.

Suitable materials to be applied as a base foil for a foil in accordance with the invention include all materials that are sufficiently biodegradable to be able to ultimately return to the environment without unacceptable stress on nature. Polymer materials that are based upon starch or cellulose, or the polymerization products of butyric acid, isobutyric acid, or one or more cyclical esters, such as lactide, glycolide, trimethylene carbonate, δ-valerolactone, β-propiolactone, or ε-caprolactone, are outstandingly well suited for this purpose. Mixtures of the stated polymer materials are likewise suitable.

In accordance with the invention, very good results are achieved with a base foil based on corn starch and polycaprolactone, whereby the quantity of corn starch amounts to 30 to 50 weight %, based upon the weight of the base foil. It has been found that this base foil itself already has favorable characteristics of permeability to oxygen- and water vapor, so that very good results are achieved with a foil that is obtained after coating this base foil with a coating layer of natural material, which coating layer lowers the permeability of the base foil to oxygen and water vapor.

A coating layer that is applied to a base foil in accordance with the invention is of a natural material. This means that the material is a natural, preferably biodegradable, base material that has possibly undergone a number of physical treatments. In this connection, one should think in terms of purifying actions. In certain

cases, the material might likewise have undergone a simple chemical treatment, such as an esterification or a hydrogenation. During such a chemical treatment, it is also usual to obtain a material that can likewise be obtained from nature, but which has another level of availability, however.

The natural materials that come under consideration for use for a coating layer in accordance with the invention are preferably selected from the group consisting of resins, natural polyesters, gelatin, hydrocolloids, fats, seasoned fats, and waxes. These materials are easily available and processable, and also have the characteristics that are desired for the invention. The materials selected from the group consisting of shellac (also termed "gumlac"), bee's wax, carnauba wax, candelilla wax, tallow, and seasoned fats on the basis of triglycerides are particularly suitable natural materials for use in the application of a coating layer to a base foil in order to obtain a foil in accordance with the invention.

The permeability of the base foil to oxygen and water vapor are lowered by the presence of the coating layer. Within the context of the invention, the oxygen permeability is defined as the quantity of oxygen that passes through 1 square meter of material with a thickness of 70 µm at a temperature of 23°C and a relative humidity of 50% within 24 hours. The determination of oxygen permeability can be measured by means of an Ox-Tran device. This device can be obtained from the company Mocon (Minneapolis, Minnesota, USA).

There is understood by "water vapor permeability" the quantity of water vapor that passes through 1 square meter of material with a thickness of 70 µm at a temperature of 23°C and a relative humidity of 70% within 24 hours. One suitable technique for the determination of water vapor permeability is the Patra method, which method has been described by Eng. P. Bange in "The measurement of the W.D.D. of packaging material" [/in Dutch/] in the journal "Verpakking" [/= "Packaging"/], April 1952, pages 34-344.

In one preferred form of implementation, the invention relates to a foil comprising a biodegradable polymer base foil to which a coating layer of natural material is applied, which coating layer, with a thickness of the foil of approx. 70 µm, lowers the permeability of the base foil to oxygen and water vapor, whereby the oxygen permeability is not greater than 100 ml/m^2 within 24 hours. It has been found that a foil in accordance with this preferred form of implementation is particularly well suited for the production of a packaging material in which goods sensitive to oxygen and/or water vapor can be preserved for a very long time. It should be clear that the storage life of a product packaged in a material made from a foil in accordance with the invention can be optimized by selecting a suitable thickness of the foil.

In accordance with another preferred form of implementation of the invention, the coating layer that is applied to the base foil also comprises a filling material. Some suitable filling materials are colloidal silica and mica.

Colloidal silica is a solution of spherical silica particles in water, which particles all have approximately the same size. The concentration of silica in the colloidal silica solution preferably amounts to between 15 and 45 weight %, based on the weight of the colloidal silica solution. It has been found that the presence of colloidal silica has a favorable influence on the permeability characteristics of a foil.

Mica is a mineral with a plate-like crystal structure. A ground mica with a small particle size, such as Mica M or Silk mica, is preferably used. The particle size preferably lies below 50 µm, particularly preferably below 15 µm.

The production of a foil in accordance with the invention is carried out by coating a biodegradable polymer base foil with a layer of natural material that is to be brought in contact, through the base foil, with an emulsion or a solution of a natural material at a temperature between 10 and 50°C, with subsequent drying.

The bringing of the base foil into contact with an emulsion or a solution of a natural material can be carried out in any appropriate manner, such as by means of brushing, for example. For an application by brushing, a base foil should be stretched on a fixed background. The application by brushing itself can be suitably carried out by means of a palette knife, or in another manner known to the technician in the area.

The natural material is preferably applied in the form of an emulsion in water. Overall, the emulsion should contain 10 to 30 weight % natural material relative to the weight of the emulsion. It is important for the emulsion to have a suitable viscosity in order to be able to be easily processed. If the emulsion has too low a viscosity, then it flows too much and is difficult to dose. If the viscosity of the emulsion is too high, then it flows too little and is difficult to apply. Given a specific natural material that is used in order to coat a base foil, the technician in the area should be able to determine a suitable viscosity.

An emulsifier can possibly be used in order to obtain a stable emulsion. Some emulsifiers that have proven to be suitable are glycerol monooleate, stearic acid, potassium hydroxide, oleic acid, and mixtures of the same, for example. The quantity of emulsifier relative to the weight of the emulsion should generally lie between 0.5 and 10, preferably between 1 and 5 weight %.

In specific cases, it is advantageous to apply the natural material in the form of a solution. A non-aqueous solution is preferably applied. Some suitable solvents are, preferably, low molecular alcohols, such as ethanol. The concentration of the solution is generally selected in such a manner that a solution contains 15 to 45 weight % of natural material, relative to the weight of the solution. It has been shown that a foil is obtained with very good characteristics upon the use of a non-aqueous solution for the application of a coating layer.

If colloidal silica are used, then these should usually be present in a quantity of 10 to 35 weight % relative to the weight of the emulsion or the solution. If a mica is used, then the quantity of mica that is present in the emulsion or the solution should mostly amount to between 4 and 18, preferably between 5 and 15 weight %, relative to the weight of the emulsion or the solution.

The bringing of the base foil incontact with the natural material takes place at a temperature of between 10 and 50°C. It has been found that the danger exists that the base foil will soften at higher temperatures, which has the result of a worsening of characteristics.

Finally, the base foil to which the natural material is applied is dried in order to remove the solvents or the fluid of the emulsion. The drying can be carried out in any appropriate manner. One possibility is formed by drying in the air.

A foil in accordance with the invention is particularly suitable for use in the production of packaging materials for the packaging of materials that are sensitive to oxygen and/or water vapor, such as walnuts, coffee, or tobacco. Such types of substances in packagings made from a foil in accordance with the invention have a sufficiently long service life. In addition, the packagings can be broken down in the environment in a natural manner once they have been discarded. In order to obtain a satisfactory storage life of the packaged good, a foil should have an overall thickness of 10 to 150 µm, preferably 25 to 100 µm, if the foil needs to be used as a base material for a packaging material.

The invention will now be explained by means of the following examples.

EXAMPLES

A foil on the basis of 40 weight % of corn starch and 60 weight % polycaprolactone, relative to the weight of the base foil, is used as the base foil (available from the company Prottera). This base foil had a thickness of approximately 50 µm. The foil is stretched, with the help of an adhesive band, on a sheet of plate glass with an underlaid pad of folded cardboard (white, coated on one side with 230 grams per square meter).

Different emulsions and solutions have subsequently been prepared for the application of a coating layer. In this connection, the compositions of the emulsions and solutions are stated in weight %, relative to the total compositions.

Example 1

Prifat no. 9833(*)	21.6%
Glycerol-monooleate	2.2%
Oleic acid	4.3%
Potassium hydroxide	0.9%
Water	71.1%

Example 2

Shellac(**)	43%
Ethanol	57%

Example 3

Shellac	30%
Ethanol	40%
Silica(***)	30%

Example 4

Shellac	38%
Ethanol	50%
Mica M	12%

(*) Prifat no. 9833 is an animal fat that can be obtained from the firm Uni Mills in Zwijndrecht, and has a melting point of 57-61°C.

(**) "Refined Bleach Shellac", which can be obtained from the company Mantrose, is used as shellac.

(***) A colloidal silica solution with a concentration of silica of 30 weight %, relative to the weight of the silica solution, is used here as a silica.

The different coating layers are applied by repeatedly stretching a portion of the base foil with an applicator which is suitable for applying a layer with a thickness of 50 µm and loaded with the various and solutions. The temperature is thereby 35°C.

The foils thus obtained are dried in the air and investigated for the permeability to oxygen and water vapor with Ox-Tran and Patra- methods, as the case may be. The results are presented in Table I below.

Table I:

Coating layer	Water vapor permeability (ml/m^2 per 24 hours)	Oxygen permeability (ml/m^2 per 24 hours)
None	123	504
Example 1	22	159
Example 2	8	118
Example 3	18	67
Example 4	8	27

CLAIMS:

1. A foil comprising a biodegradable polymer base foil to which a coating layer of natural material is applied, which coating layer lowers the permeability of the base foil to oxygen and water vapor.

2. A foil in accordance with claim 1, whereby the oxygen permeability is not greater than 100 ml/m^2 per 24 hours at a thickness of the foil of approximately 70 µm.

3. A foil in accordance with one of the preceding claims, whereby the base foil is based on starch, cellulose, or a polymerization product of butyric acid, isobutyric acid, or one or more cyclical esters, or a mixture thereof.

4. A foil in accordance with claim 3, whereby the base foil is based upon corn starch and polycaprolactone, whereby the quantity of corn starch amounts to 30 to 50 weight %, based upon the weight of the base foil.

5. A foil in accordance with one of the preceding claims, whereby the natural material is selected from the group consisting of resins, natural polyesters, gelatins, hydrocolloids, fats, seasoned fats, and waxes.

6. A foil in accordance with claim 5, whereby the natural material is selected from the group consisting of shellac, bee's wax, carnauba wax, candelilla wax, and seasoned fats on the basis of triglycerides.

7. A foil in accordance with one of the preceding claims, whereby the coating layer likewise includes a filling material.

8. A foil in accordance with claim 7, whereby the filling material is colloidal silica or mica.

9. A process for the production of a foil in accordance with claim 1 to 8, whereby a biodegradable polymer base foil is coated with a layer of natural material by bringing the base foil into contact with an emulsion or a solution of a natural material at a temperature of between 10 and 50°C and is thereupon dried.

10. A process in accordance with claim 9, whereby the base foil is brought into contact with an emulsion.

11. A process in accordance with claim 10, whereby the emulsion includes an emulsifier.

12. A process in accordance with claim 11, whereby the emulsifier is selected from the group consisting of glycerol monooleate, stearic acid, potassium hydroxide, oleic acid, and mixtures thereof.

13. The application of a foil in accordance with claim 1 to 8 for the production of a packaging material for the packaging of materials that are sensitive to oxygen and/or water vapor.

COOPERATIVE TREATY (PCT)
REPORT CONCERNING
THE INVESTIGATION OF INVENTIVE ACTIVITY OF THE INTERNATIONAL TYPE

Identification of the national application:	Identification of the applicant or authorized representative of the same: **NW 1197**
Dutch application no. **1006548**	Date filed **July 10, 1997**
	Priority date claimed
Applicant (name) **SARA LEE / DE N.V.**	
Date of the request for the search of the international type **—**	The International Search Authority hereby assigns the petition for a search for the ... /illegible/ ... the number: **SN 29859 NL**

I. CLASSIFICATION OF THE SUBJECT (upon use of different classifications, state all classification symbols):

In accordance with the international classification (IPC)
Int. Cl. 6: C 08 J 7/04

II. AREAS OF TECHNOLOGY SEARCHED

Minimum documentation searched

Classification system	Classification symbols
Int. Cl. 6	**C 08 J**

Documentation other than the minimum documentation searched, insofar as such types of documents are included in the areas searched.

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III. ☐ NO SEARCH POSSIBLE FOR SPECIFIC CLAIMS (notes on supplemental sheet)

IV. ☐ LACK OF UNITY OF THE INVENTION (notes on supplemental sheet)

REPORT ON THE INVESTIGATION OF INVENTIVE ACTIVITY OF THE INTERNATIONAL TYPE	Number of the petition for an investigation of novelty **NL 1006548**

A. CLASSIFICATION OF THE SUBJECT:
IPC 6 C08J7/04
In accordance with the International Patent Classification (IPC), as well as the national classification in accordance with the IPC.

B. AREAS OF THE TECHNOLOGY SEARCHED

Minimum documentation searched (classification followed by classification symbols)
IPC 6 C08J

Documentation searched other than the minimum documentation for such types of documents, insofar as such types of documents are included in the areas searched.

Electronic databases consulted during the international investigation of novelty (name of the data bases and, where possible, key words used)

C. DOCUMENTS CONSIDERED TO BE OF IMPORTANCE

Category(*)	Documents cited, possibly with indication of passages of particular importance	Important for claim no.
	WO 93 11937 A (NOVAMONT S.P.A.) - June 24, 1993 See claims 1, 3, 4, 7, 8, 10, 15 See page 1, paragraph 1 See page 3, lines 10-15 See page 4, lines 18-26 See page 5, lines 13-14 See page 7, lines 5-8 See page 8, lines 1-7 See Example 2 See page 14, lines 26 - Page 15, line 2	1, 3-11, 13.

☑ Additional documents are noted in the continuation of box C.
☑ Members of the same patent family are noted in an appendix.

(*) Special categories of documents cited.

"A"	Document which reproduces the general state of the art but is not considered to be of particular importance.	"T"	Later document, published after the date of filing or priority date and not in conflict with the application, but cited for clarification of the principle or the theory which lies at the basis of the invention.
"E"	Earlier document, but published on the date of filing or thereafter.	"X"	Document of particular importance; the document for which exclusive rights are applied can not be considered to be novel, or can not be considered to be based upon inventive activity.
"L"	Document which appeals to a priority right of ... /illegible/ ..., or which is cited in order to determine the publication date of another citation or another reason than stated.	"Y"	Document of particular importance; the invention for which exclusive rights are applied can not be considered to be inventive if the document is considered in combination with one or more similar documents, and this combination is obvious for an expert.
"O"	Document that relates to an oral explanation, a use, an exhibition, or another means	"&"	A document which forms a part of the same patent family.
"P"	Document published before the date of filing but after the priority date claimed.		

/Completion of previous page/:

Date on which the investigation of novelty of the international type was completed. **March 4, 1998**	Date of submission of the report of the investigation of novelty of the international type
Name and address of governmental body **European Patent Office** **P.S. 5816** **Patentlaan 2** **NL 2280 HV Rijswijk** Tel.: (+31-79) 340-2040 Telex: 31 651 epo nl Fax: (+31-70) 340-3016	Authorized official **Hallemeesch A.**

REPORT ON THE INVESTIGATION OF INVENTIVE ACTIVITY OF THE INTERNATIONAL TYPE	Number of the petition for an investigation of novelty **NL 1006548**

C. (Continued) DOCUMENTS CONSIDERED TO BE OF IMPORTANCE

Category(*)	Documents cited, possibly with indication of passages of particular importance	Important for claim no.
"X"	WO 94 13734 A (FRANZ HAAS WAFFELMASCHINEN INDUSTRIEGESELLSCHAFT MBH) - June 23, 1994 See claims 1-6 See page 1, paragraph 1 See page 22, substrate F See Examples 6, 7	1, 3, 5, 6, 9, 13
"X"	GB 375 194 A (WOLFF & CO., KOMMANDIT-GESELLSCHAFT AUF AKTIEN) - January 23, 1932 See claim 5 See page 1, lines 64-92 See page 2, lines 16-32	1, 3, 5, 6
"X"	GB 472 265 A (BRITISH CELLOPHANE LIMITED) September 20, 1937 See claims 1-3 See page 1, lines 82-92 See Example 1	1, 3, 5, 6, 9
"A"	US 5 462 983 A (S. BLOEMBERGEN ET AL.) - October 31, 1995 See claims 1-13	1, 3, 4

REPORT ON THE INVESTIGATION OF INVENTIVE ACTIVITY OF THE INTERNATIONAL TYPE

Information on the members of the same patent family

Number of the petition for an investigation of novelty

NL 1006548

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